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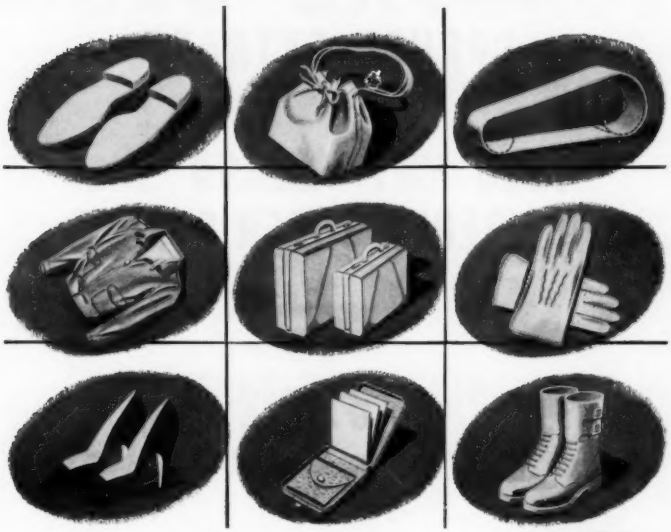

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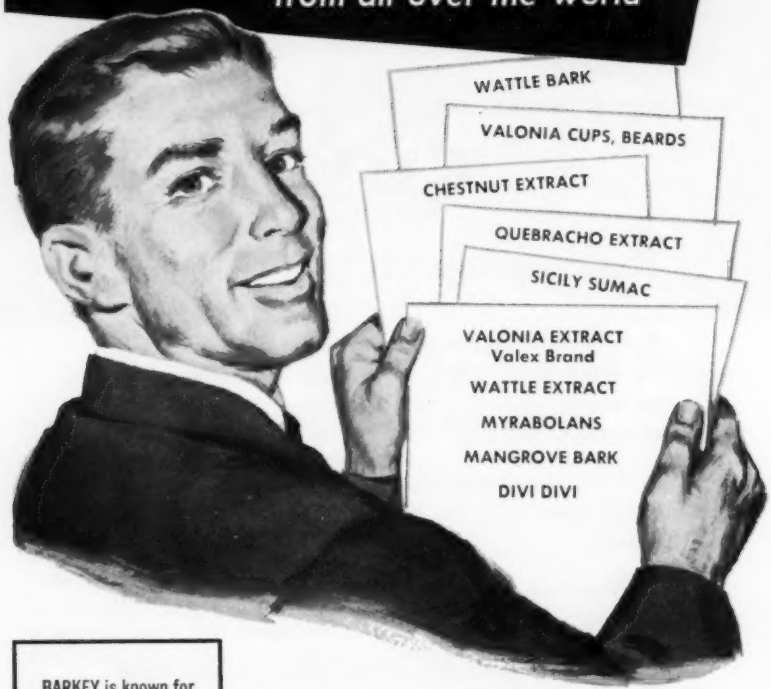

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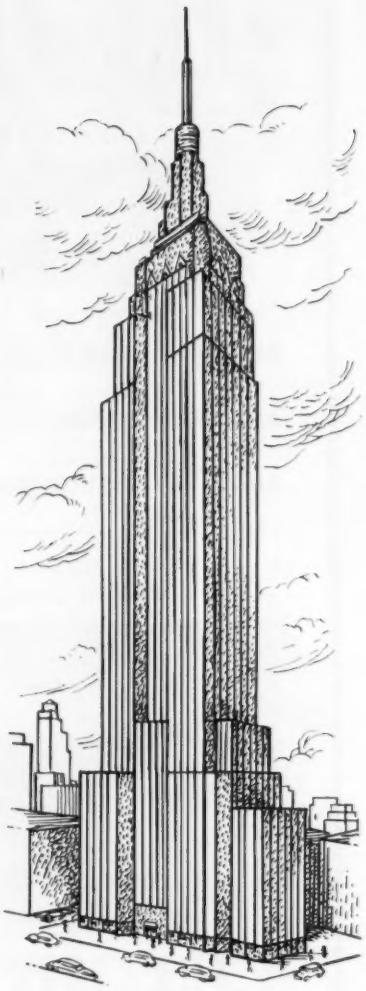

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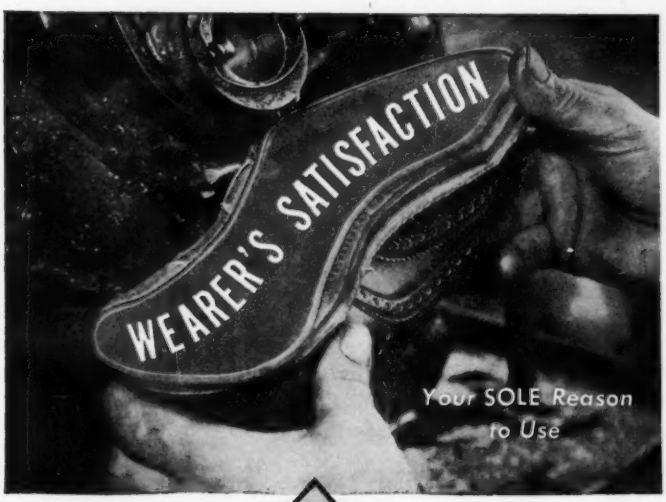

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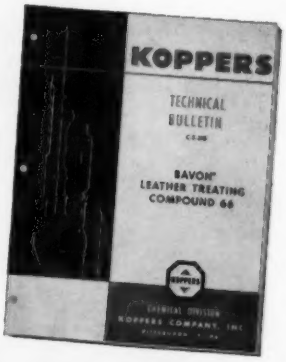

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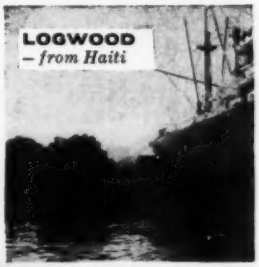

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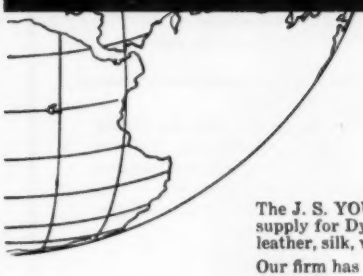

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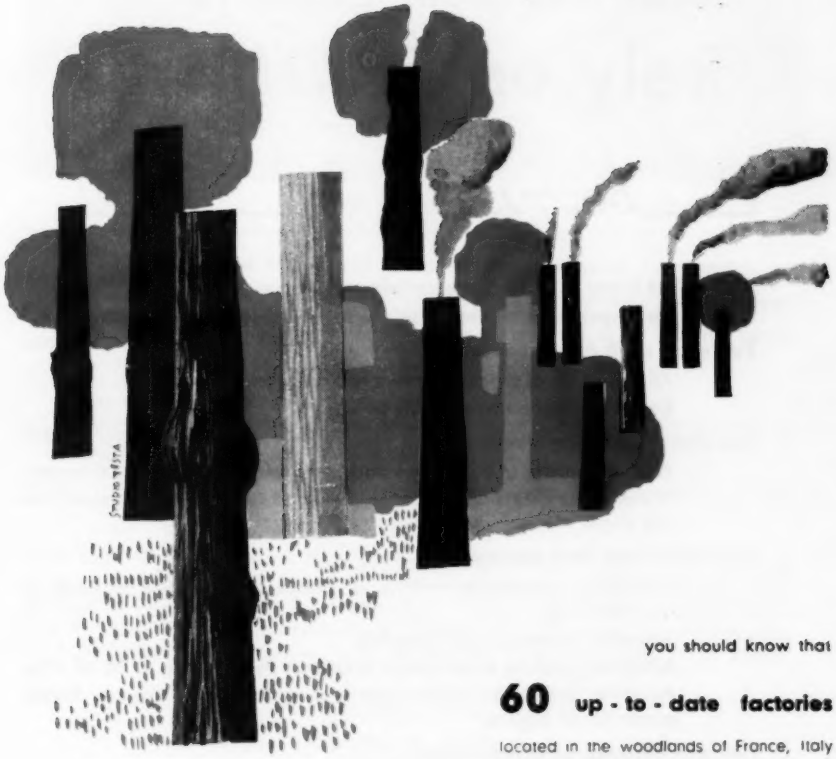

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Statistical Study of Tannin and Sampling*

By R. C. PUTNAM, C. B. CRANDALL** and E. FACER, JR.

United States Testing Company, Inc.
Hoboken, New Jersey

ABSTRACTS

A series of tannin shipments have been sampled in duplicate and analyzed. The duplicate samples were obtained from different bags in the same lot. A computation has been made of the net variation between bags. Using this information, a statistical sampling plan has been designed, which yields a constant allowable uncertainty of the sample average regardless of lot size, which is not the case with the Official or Tentative Methods.

The tannin analyses of the duplicate samples from twenty lots have been performed in duplicate and the variance compared with that allowed by the Official Method.

A vast amount of labor has been expended in the past in the development of the A.L.C.A. Method of Tannin Analysis. Much of the work was concerned with the technique, equipment, and materials used in the procedure. Various laboratories participated in the studies and general comparisons were made of the data obtained. However, it appears that no adequate statistical treatment of the data was undertaken to supply information on the errors of sampling and analysis. This paper describes studies carried out in one laboratory to obtain such information for the sampling and analysis of quebracho tannin by the Official Method.

PROCEDURE

Twenty representative lots of quebracho tannin were sampled in duplicate in accordance with the sampling schedule and procedure specified in the Official Method. From each of the specified number of bags, randomly selected from a lot, was drawn a single portion. The composite of all the portions constituted the first gross sample. This operation was repeated on another set of bags in the lot to obtain a second gross sample. Each gross sample was analyzed in duplicate.

DATA AND STATISTICAL ANALYSIS

The analytical data, in per cent tannin content, are given in Table I. The analysis of variance of these data is summarized in Table II. Based on the estimates of the components of variance thus obtained, conclusions may be drawn as follows:

*Presented at the Fifty-first Annual Meeting, Swampscott, Mass., May 23, 1955.
**Present address: Burlington Industries, Cramerton, S. C.

TABLE I

Lots	Samples I, Analyses A	Samples I, Analyses B	Samples II, Analyses A	Samples II, Analyses B
1	63.82	63.57	63.55	63.47
2	69.30	69.25	68.56	68.07
3	65.47	65.40	64.09	64.34
4	64.81	64.92	64.32	64.09
5	64.38	63.87	64.30	64.13
6	67.76	67.15	68.60	68.15
7	61.95	62.00	63.87	64.22
8	63.88	64.38	63.95	63.69
9	64.47	64.59	65.58	65.37
10	66.12	66.15	65.97	66.49
11	63.05	63.13	64.21	64.40
12	64.35	65.23	64.17	63.70
13	62.67	63.11	63.92	63.80
14	65.27	64.97	65.28	64.89
15	63.91	64.29	64.73	64.35
16	63.45	63.03	62.72	63.34
17	62.62	62.85	61.82	62.98
18	64.27	63.87	65.83	65.89
19	65.02	65.12	64.85	64.20
20	64.25	64.60	63.82	63.50

TABLE II

Analysis of Variance

Source of Variation		Mean Square	Variance	Standard Deviation
Lots	$S_a^2+2S_s^2+4S_L^2$	= 9.4448	S_L^2 = 2.1536	1.47
Samples	$S_a^2+2S_s^2$	= 0.8302	S_s^2 = 0.3736	0.61
Analyses*	S_a^2	= 0.0830	S_a^2 = 0.0830	0.29

L-between lots s - between samples a - between analyses

*S_a^2 includes any effects due to selecting test specimens from the gross sample. These effects have been shown in a separate study to be negligibly small.

1. The 95% confidence limits for the average of duplicate analyses on the same sample by one laboratory is $\frac{tS_a}{\sqrt{2}} = \frac{1.96 \times .29}{\sqrt{2}} = \pm 0.40\%$

2. The average difference between duplicate analyses is estimated as $d_2S_a = 1.128 \times 0.29 = 0.32\%$. This difference will be exceeded about half the time. A difference of $1.96 \times .29 \times \sqrt{2} = 0.80\%$ is expected to be exceeded about 5 per cent of the time. Both the Official and Provisional Methods

state that duplicate analyses are in good agreement if they do not differ more than 0.3 per cent. It is obvious that such a requirement would be too stringent.

3. If each of two laboratories drew an independent gross sample and analyzed it in duplicate, the difference between their average results should not be considered significant unless it exceeded

$t\sqrt{\frac{2(S_s^2+S_a^2)}{2}}=1.96\sqrt{\frac{2(.3736+.0830)}{2}}=1.78$ per cent, assuming equal sampling and analytical precisions.

4. The increase in the precision of a determination of the tannin content of a lot that results from performing the analysis in duplicate is negligible. For a single test, the precision at the 95 per cent confidence level is

$t\sqrt{S_s^2+S_a^2}=1.96\sqrt{.3736+.0830}=1.32$ per cent. For the average of duplicate tests, the precision is $1.96\sqrt{\frac{.3736+.0830}{2}}=1.26$ per cent

Little is accomplished by the running of duplicate analyses except the detection of gross errors.

The data in Table I may be further analyzed to give an estimate of the variation in per cent tannin content of the individual portions composing a gross sample by means of the following equation:

$$S_q^2 = \frac{\sum^{M} n_i d_i^2}{4M} - \frac{S_a^2 \sum^{M} n_i}{2M}$$

where

S_q^2 = estimate of the variance in quality between the individual portions (one per bag) composing the gross sample, corrected for analytical error

n_i = total number of bags sampled in the i-th lot (twice the number per duplicate gross sample)

d_i = difference between the average tests on the duplicate gross samples from the 1-th lot

M = number of lots

S_a^2 = estimate of the variance of a single analysis.

Applying the data of Table III in this equation, we find

$$S_q^2 = \frac{548.2322}{80} - \frac{.0830 \times 674}{40} = 5.4543$$

TABLE III

Lot	na	Sample I (Av.)	Sample II (av.)	da	nada²
1	52	63.70	63.51	0.19	1.8772
2	38	69.28	68.32	0.96	35.0208
3	38	65.44	64.22	1.22	56.5592
4	38	64.87	64.21	0.66	16.5528
5	20	64.13	64.22	0.09	0.1620
6	42	67.46	68.38	0.92	35.5488
7	20	61.98	64.05	2.07	85.6980
8	20	64.13	63.82	0.31	1.9220
9	36	64.53	65.48	0.95	32.4900
10	64	66.14	66.23	0.09	0.5184
11	24	63.09	64.31	1.22	35.7216
12	20	64.79	63.94	0.85	14.4500
13	28	62.89	63.86	0.97	26.3452
14	16	65.12	65.09	0.03	0.0144
15	20	64.10	64.54	0.44	3.8720
16	52	63.24	63.03	0.21	2.2932
17	38	62.74	62.40	0.34	4.3928
18	54	64.07	65.86	1.79	73.0214
19	34	65.07	64.53	0.54	9.9144
20	20	64.43	63.66	0.77	11.8580
	674				548.2322

Sampling Plan

Tanner and Deming[1] have presented a statistical sampling plan for use on bulk materials which permits the sampling of a lot of bulk material for the determination of an average quality characteristic at minimum cost. For this purpose a formula is used for calculating the size of a sample having the required precision. This formula is based on the variance of the quality of individual portions within a package, S_w^2, and the variance of the quality between packages in a lot, S_b^2. Their method has been applied in the sampling of many commodities, notably packaged raw wool[2]. Tanner and Lerner[3] have presented a procedure for obtaining, economically, current estimates of S_w^2 and S_v^2 in the course of routine analysis of duplicate composite samples. If only a single portion per package is to be used in obtaining a composite sample, as is the present practice with tanning materials, a simple adaptation of their plan may be used.

The adaptation is essentially the procedure followed in this work. One-half of the required number of portions (one per bag) are composited to form the first gross subsample, and the remaining portions are composited to form the second gross subsample. Each of these subsamples is then analyzed in duplicate. From the accumulated analytical data estimates of S_q^2 and S_a^2

may be obtained as described in the preceding section. These estimates may be used for determining required sample size to give the desired precision and in the control of analytical errors in the laboratory.

The required total sample size may be calculated from the following formula:

$$n = \frac{NS_q^2}{\left(\frac{E}{t}\right)^2 (N-1) + S_q^2}$$

where

n = total number of bags to be sampled in a lot
N = number of bags in a lot
E = allowable uncertainty of the sample mean
t = probability factor

The sampling schedule in A.L.C.A. Provisional Method of February, 1954,[4] does not provide equal sampling precision for lots of different size. For example, it requires that 6 bags be sampled from a lot of 61 to 84 bags, which will give a sampling error of ±1.8 per cent tannin at the 95 per cent confidence level, whereas for a lot of 2521 to 2660 bags it requires that 36 bags be sampled, in which case the sampling error is only ±0.8 per cent tannin. A sampling schedule based on constant sampling error regardless of lot size is in many respects advantageous. For illustrative purposes, such a schedule, based on an allowable constant error of ±1.2 per cent at a confidence level of 95 per cent and on the value of S_q^2 of 5.4543 as found in this study, is shown in Table IV. This may be compared with the A.L.C.A. Provisional Method schedule given in Table V[4].

TABLE IV

Constant E Schedule

Number of Bags in Lot	Number of Bags to be Sampled
1 – 4	Each
5	4
6 or 7	5
8 or 9	6
10 – 12	7
13 – 16	8
17 – 21	9
22 – 29	10
30 – 41	11
42 – 62	12
63 – 109	13
110 – 306	14
307 – 10,000	15

TABLE V

A.L.C.A. Provisional Method

Number of Bags in Lot	Number of Bags to be Sampled
1 – 3	Each
3 – 24	3
25 – 40	4
41 – 60	5
61 – 84	6
85 – 112	7
113 – 144	8
145 – 180	9
181 – 220	10
221 – 264	11
265 – 312	12
313 – 364	13
365 – 420	14
421 – 480	15
481 – 544	16
545 – 612	17
613 – 684	18
685 – 760	19
761 – 840	20
841 – 920	21
921 – 1010	22
1011 – 1100	23
1101 – 1200	24
1201 – 1300	25
1301 – 1400	26
1401 – 1510	27
1511 – 1640	28
1641 – 1730	29
1731 – 1860	30
1861 – 1980	31
1981 – 2100	32
2101 – 2240	33
2241 – 2380	34
2381 – 2520	35
2521 – 2660	36
2661 – 2810	37
2811 – 2960	38
2961 – 3120	39
3121 – 3280	40
3281 – 3440	41
3441 – 3610	42
3611 – 3780	43
3781 – 3960	44
3961 – 4140	45
4141 – 4320	46
4321 – 4550	47
4551 – 4700	48

TABLE V (Continued)

A. L. C. A. Provisional Method

Number of Bags in Lot	Number of Bags to be Sampled
4701 – 4900	49
4901 – 5100	50
5101 – 5300	51
5301 – 5520	52
5521 – 5720	53
5721 – 5940	54
5941 – 6160	55
6161 – 6380	56
6381 – 6600	57
6601 – 6840	58
6841 – 7080	59
7081 – 7320	60
7321 – 7560	61
7561 – 7800	62
7801 – 8060	63
8061 – 8320	64
8321 – 8580	65
8581 – 8840	66
8841 – 9120	67
9121 – 9400	68
9401 – 9660	69
9661 – 10,000	70

As stated above, the proposed plan of taking duplicate gross subsamples in the manner described enables us to obtain an estimate of S_q^2 for each lot. The accumulated data is helpful in designing sampling schedules. In addition, the plan enables us to use a control chart for sampling, similar to that described for analyses in the following section.

Control Charts

When duplicate analyses are used as a control over gross analytical errors, it is convenient to determine upper and lower control limits for the difference between duplicates and check the results obtained against the controls. The limits may be drawn on a range chart if desired, and the differences plotted as found. This eliminates the need for computation and as long as the points fall within the limits set, there is no lack of control. In Table VI are given the differences between duplicate analyses for the duplicate samples from the twenty lots with respect to moisture, total solids, soluble solids, non-tannins and tannins. The A.L.C.A. analytical methods[4] with differences between duplicates considered to be in good agreement, are as follows:

TABLE VI

Differences Between Duplicates

	Moisture	T. S.	Ins.	S. S.	N. T.	T.
1	.06	.06	.24	.18	.43	.25
	.05	.05	.05	.10	.02	.08
2	.20	.20	.45	.25	.30	.05
	.19	.19	.08	.11	.38	.49
3	.02	.02	.18	.16	.09	.07
	.07	.07	.08	.15	.10	.25
4	.06	.06	.20	.26	.25	.51
	.18	.18	.01	.17	.00	.17
5	.38	.38	.19	.57	.07	.50
	.10	.10	.18	.08	.18	.26
6	.37	.37	.98	.61	.00	.61
	.00	.00	.38	.38	.07	.45
7	.50	.50	.45	.05	.00	.05
	.36	.36	.39	.03	.38	.35
8	.07	.07	.73	.80	.08	.88
	.33	.33	.58	.25	.22	.47
9	.20	.20	.50	.30	.42	.12
	.46	.46	.03	.43	.22	.21
10	.30	.30	.05	.35	.32	.03
	.10	.10	.20	.30	.22	.52
11	.18	.18	.43	.25	.17	.08
	.06	.06	.06	.00	.19	.19
12	.03	.03	.26	.29	.09	.38
	.07	.07	.21	.28	.10	.38
13	.17	.17	.74	.57	.13	.44
	.37	.37	.32	.05	.07	.12
14	.03	.03	.45	.48	.18	.30
	.05	.05	.13	.18	.21	.39
15	.10	.10	.21	.11	.27	.38
	.22	.22	.43	.21	.17	.38
16	.01	.01	.54	.53	.09	.62
	.03	.03	.47	.44	.02	.42
17	.37	.37	.07	.30	.07	.23
	.17	.17	.68	.85	.31	1.16
18	.16	.16	.66	.50	.10	.40
	.18	.18	.07	.11	.17	.06
19	.02	.02	.11	.13	.23	.10
	.20	.20	.30	.50	.15	.65
20	.04	.04	.28	.24	.11	.35
	.05	.05	.53	.48	.16	.32
$\bar{R}$	.163	.163	.323	.299	.169	.338
U.C.L.	0.53	0.53	1.06	0.98	0.55	1.10

1. Total Solids—Solution with insolubles, mixed and evaporated (0.2)
2. Moisture—100 minus total solids

3. Soluble Solids—Solution with insolubles mixed, filtered and evaporated (0.2)

4. Insolubles—Total solids minus soluble solids

5. Non-tannins—Solution with insolubles mixed, treated with hide powder, filtered, insolubles filtered, and evaporated (0.2)

6. Tannins—Soluble solids minus non-tannins (0.3)

In Table VI are given the mean ranges ($\bar{R}$) obtained from the analyses of duplicates. Upper control limits have been computed using the formula $D_4\bar{R}$ where $D_4 = 3.267$. The limit chosen is three standard deviations of the sampling distribution of the range, $\bar{R}$, for duplicate observations. Industrial applications of control charts have shown this to be a suitable factor. A comparison of the values in the range chart with the corresponding U. C. L. values showed only one instance of lack of control. This was in the difference between duplicates in sample 17II. Both the soluble solids and non-tannin analyses were in control, but the difference value for the former was close to the control limit. When combined with the non-tannin value, it placed the tannin difference out of control. The advantage of using control limits or control charts for deciding if a difference between duplicates is significant, and if analyses should be repeated, is self-evident.

Since the A.L.C.A. values for differences between duplicates, which are considered to be in good agreement, are much lower than the control limits (Table VII), it is obvious that these values are too stringent. The control limits are based on a representative group of lots of quebracho tannin and may be used as they stand as criteria for the tannin analysis procedure.

TABLE VII

Differences Between Duplicates

	U. C. L.	A. L. C. A. ("Good Agreement")
Moisture	0.53	
Total Solids	0.53	0.2
Insolubles	1.06	
Soluble Solids	0.98	0.2
Non-tannins	0.55	0.2
Tannins	1.10	0.3

Summary

1. The variance in sampling and analysis of quebracho tannin has been calculated and confidence limits determined.

2. An improved schedule for sampling quebracho tannin has been presented.

3. Data for use in preparing control charts have been given and compared with A.L.C.A. "good agreement" values.

The authors wish to express their gratitude to Mr. Louis Tanner, Chief Chemist of the U. S. Customs Laboratory, Boston, Massachusetts, for his helpful suggestions and revision of the manuscript.
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   a. Official Method
   b. Provisional Method, February, 1954.

Discussion

Mr. Kay, (Howes Leather Company): I do not know how we happen to get the Chairman of the Vegetable Leathers Committee and of the Tannin Analysis Committee to discuss this paper. I imagine the Tanners Council has some idea on the subject. When these methods were rewritten in 1954 the Committee realized that the original sampling schedule was purely empirical. I don't know when that was originally devised. It was away back in the dim and distant past.

We did approach a couple of statisticians to try and devise a formula. They reported back that with the information then available, no such formula was possible.

The British procedure, as some of you know, uses the root of N/2 and I took the trouble to write them and they tell me that they have no statistical basis for that figure, either.

Commercial people said, "Well, we need more samples at the low range and not quite as many at the high range." And the root of N/2 gave a satisfactory agreement.

Therefore we accepted that and that was the way the basis for that table came about. It is not statistical and I am glad to see a statistical approach to it. I hope we will get something worked out on this.

I did have the privilege of seeing the paper earlier and I had a chance to look it over. I am no statistician. But I detect in it, I think, using Dr. Putnam's figures, two errors in his second equation there. According to my

calculations, instead of 1.2, I get 1.9, and instead of 2.4, I get 1.8. That is a slip and of course only a minor matter.

Dr. Putnam says our ALCA empirical agreement between duplicates is much too stringent. I think I speak for the people who analyze vegetable tannins when I say we can all get within those limits, both between duplicates and between laboratories, a great deal better than 50 per cent of the time.

The ALCA limits between laboratories are 1.5 per cent of the mean tannin. As I understand Dr. Putnam's figures, the sampling error alone is greater than that.

Again I can only say that we do not find it in practice.

I am not going to discuss the statistics. I am not qualified to do so. But I would like to ask Dr. Lollar if he would care to pass a little comment on this—if he has anything to say about the statistical side.

DR. LOLLAR: First, I would like to say that I would thank Dr. Putnam and his group for bringing before us some data which we can consider to reflect the total sources of variability in the tannin analysis.

Certainly the laboratory error is only a part of it and we do need to get all of it. The other factor which Arthur specifically asked about—that of the replicate or duplicate analysis error, I have discussed that with Arthur Kay earlier this morning and if the laboratories who are doing the work are getting a lower figure, I think we should examine those routine figures as they are secured, set up a control chart on those figures, and see whether there may be a between-laboratory difference which then we need to study.

Certainly we want the best information that we can get on the duplicate error. And if they are not constant between laboratories, then we should find out why they are not constant. I have already said to Arthur that if he will supply additional data, I should like to look at them in comparison to these, to see what they may indicate.

KAY: Mr. Presley?

MR. ELWOOD E. PRESLEY, (Eagle-Ottawa Leather Company): We appreciate the amount of work that has been done by Mr. Putnam and his coworkers. This statistical approach to our sampling method and suggested sampling table is very interesting. The constant table "E" that you had on the chart, or on the board here, sir—the lots from 110 to 306, you showed 14 bags to be sampled. Is that 14 or 28?

DR. PUTNAM: Twenty-eight.

PRESLEY: And from 700 to 10,000 bags, it is 15, or a total of 30. Do you feel that in a 10,000-bag lot in which there are innumerable different manufacturing lots, that in sampling only 30 bags, taking 10,000 as the maximum figure—do you feel that this is actually a sampling that will give you your true value?

PUTNAM: It will give the value within the precision that we have requested here—1.2 per cent, based on these data showing what the general variance is in the examples that we have of 20 lots here.

The advantage of this plan is that if lots were to vary greatly in the future, you would discover it and the plan allows for the constant adjustment of the sample to that. There would not be a great adjustment, but there would be some. Whereas, under the present system there are no data available. You do not find it out as you go along and so no change is made in the sampling plan.

In other words, this allows a constant correction as time goes on, of the data which have been based on an earlier estimate of the variance.

PRESLEY: In your chart, in smaller lots such as 10 to 12 bags to the lot, you sample 7 twice, or a total of 14 bags. And yet you only have a total of 12 bags.

PUTNAM: Obviously you cannot sample more than you have.

PRESLEY: Is it just the way the factors work out according to the table?

PUTNAM: That's right.

PRESLEY: Going back to Arthur's remarks, in regard to the ALCA sampling chart, this work is certainly an indication that possibly our ALCA method should be reexamined. The data presented here are just from one laboratory and it might be advisable that the sampling procedure be examined possibly through some committee work.

Are there any other questions from the floor?

Mr. C. D. WILSON (Fred Rueping Leather Co.): Did I understand you to imply, at least, that the control charting of lots would relieve one of the need for having variable UCL and LCL? Could it be a constant upper and lower control limit because of this detail of constant precision?

PUTNAM: The values that were given here give you the upper control limit.

WILSON: Regardless of the lot size?

PUTNAM: Yes.

WILSON: That would seem a distinct advantage in itself because there is nothing so cumbersome as a control chart with variable control limits, especially if you are preserving data and plotting it weekly or daily.

PUTNAM: If these data were accepted and could be combined with data from other laboratories, the advantage is that they could serve as the standard until more data are collected and future lots came into the country

that showed enough difference to make it worth changing the control limits or the sampling numbers.

KAY: I would like to add one thing along the line of Dave Wilson's comment: there is also an economic aspect to this sampling. The members of our Committee who are trade analysts and versed in that matter tell us the bulk of the cost of sampling lies in sending somebody down to a pier, cutting open the bags—and somebody has to sew the bags up, which is quite a factor. And the smaller the lot, the greater the proportionate cost. It has brought home to us by these men, who are rather experienced, that it was desirable not to increase the number of samples on a small lot unduly. Otherwise you run into this rather excessive economic aspect.

PUTNAM: I might add that while I did not put it into the paper, by the addition of one or two simple formulas which mean just taking the cost of taking a sample and the cost of a tannin analysis, these data can be fed through and you can come out with what would be the best plan.

In other words, you could see whether or not you are willing to pay that cost. If not, you can see how much precision you would like to have, versus the cost for obtaining it.

Studies of the Chrome Tanning Process*

I. STRESS-STRAIN STUDIES ON TANNED KTT

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ABSTRACT

Hydrothermally shrunken chrome tanned kangaroo-tail tendon has been shown to obey the requirements of the kinetic theory of rubber elasticity. Using the stress-strain technique it has been possible to follow the chrome tanning process insofar as it leads to thermally stable crosslinks.

Relationships between the basicity and equilibrium pH of chrome liquors, the degree of crosslinking and pH, the degree of crosslinking and bound chromium, the degree of crosslinking and shrink temperature, the shrink temperature and bound chromium, as well as the effect of liming, deliming and pickling are presented. Extension of the present approach to additional aspects of the chrome tanning process is indicated.

*Presented at the Fifty-first Annual Meeting, Swampscott, Mass., May 23, 1955.

Introduction

The chrome tanning process has been, for many decades, the center of intense commercial and scientific interest which has led to an enormous amount of technological and academic study and investigative effort. To this day, however, no completely satisfactory picture has been presented of the highly complex physical and chemical transitions occurring during this process. Mention should be made of the very important contributions of Stiasny [1], Gustavson[2a], Shuttleworth [3], Küntzel [4] and others to our understanding of the chrome liquor. On the nature of the interactions of chrome solutions with collagen based on protein composition and structure we are indebted to Bowes[5a], Lloyd [6], Highberger [7], Merry [8], Weir [9], Sykes [10], as well as others in this country and abroad. However, notwithstanding the high level of these many efforts we are still in the "bits and pieces" stage where fresh concepts and techniques may assist in the integration and coordination of our present status of knowledge of the chrome tanning process.

The newer theories and techniques of the physical chemistry of macromolecules and inorganic complexes offer promise for the rational and systematic clarification of protein and mineral tan structure and function. The kinetic theory of rubber elasticity seems a far cry from chrome tanned leather but the initial researches of Wiederhorn and coworkers [11] have shown that hydrothermally shrunken collagen, both untanned and formaldehyde tanned, does in fact conform quite closely to the requirement of the rubber theory [12, 13, 14] in its stress-strain properties. The work reported in this paper was based on an effort to extend this approach to the problem of chrome tanning. Particular emphasis was laid on relating the degree of crosslinking and the pH of the tanning solution to the conventional parameters of shrinkage temperature and fixed chromium content. Assumptions in accord with interpretations given by Stiasny [4], Gustavson[2b] and others [3, 9, 10], were made as to (1) the participation of ionized carboxyl groups as crosslinking sites, (2) the predominantly cationic character of the chrome complexes, (3) the thermal and chemical stability of the chrome crosslink, and (4) the sequence of attachment, crosslinking and plumping reactions.

It should be pointed out that the behavior of hide protein, in its relatively open fibrous form, subject to severe mechanical stresses during tanning, may be significantly different from that of kangaroo-tail tendon, a relatively dense closely packed form of collagen. However, it is believed that the physicochemical behavior of collagen in the presence of chrome complexes should have the same main features in all collagenous tissue.

Experimental

1. The kangaroo tail tendons (KTT) used in these studies were obtained from commercial suture sources as dry bundles of untreated tendons. The

KTT was treated with 10 per cent sodium chloride solution for several days until no soluble protein nitrogen was detected. The salt extracted KTT was then rinsed in many changes of distilled water at room temperature until no test for chloride ion was obtained in the wash water. After air drying, the KTT was extracted for 24 hours, in a Soxhlet apparatus, with diethyl ether to remove fatty material. The "purified" KTT was then stored, air-dry, until needed. Before tanning, the KTT was soaked in a "salt-pickle" solution (0.75 per cent H_2SO_4, 12.5 per cent Na_2SO_4) for a minimum of 24 hours. Experiment showed that "pickling" for over 168 hours had no effect on the ultimate stress-strain data.

2. Chrome tanning was carried out in stoppered test tubes with continuous shaking for 24 hours. An average weight of 1 gram of KTT per 13.4 ml. of tanning liquor was taken (ca. eight tendons in 40 ml.). These values were taken as a compromise between commercial tanning hide : liquor ratios and the necessity of covering the KTT with liquor. The basic tanning solutions were made from $Cr_2(SO_4)_3.8.67\ H_2O$ with calculated additions of Na_2CO_3 to give the required basicities. The primary solution was made to 0.75 per cent Cr_2O_3, adjusted to 33-1/3 per cent basicity and aged for seven days. pH measurements were made with a Beckman Model G glass electrode pH meter.

The tanning procedure was to shake the KTT for two hours in the 33-1/3 per cent basic solution after which additions of Na_2CO_3 were made every two hours to the appropriate test tubes until the desired basicity in each tube was attained. Shaking was then continued for a total tendon : liquor contact time of 24 hours.

3. The tanned KTT was removed from the tanning test tubes, placed in cheese-cloth bags, and rinsed in running tap water for 24 hours. After washing in distilled water the tanned KTT was stored in distilled water before shrinkage for stress-strain measurements.

4. The hydrothermal shrinkage process was uniformly carried out in boiling water for not more than thirty seconds for untanned KTT; for tanned KTT three minutes was required. The shrunken KTT was then mounted in the stress-strain clamps and allowed to remain in the water bath at the temperature of measurement, under no applied tension, for 4 hours. A four hour period had been previously determined to be sufficient for attaining equilibrium values.

5. The stress-strain measurements were run in a distilled water bath at several temperatures held constant to (±0.1°C.). Maximum extension was 15 per cent of the zero-stress length and was attained by 1 mm. extensions made at 2.5 minute intervals. This schedule had been previously determined to give minimum hysteresis and good reproducibility. Each sample was measured at least twice following the above procedure. A slight permanent

extension of about 1 mm, after the first run, was noted after relaxing the stretched sample. The length between clamp faces ranged from 6 to 9 cm.

6. The stress-strain apparatus was substantially modified from that described previously [11]. The diagrammatic sketch (Figure I) indicates the important parts of the equipment. Greatly improved precision and convenience have resulted from the use of the present arrangement.

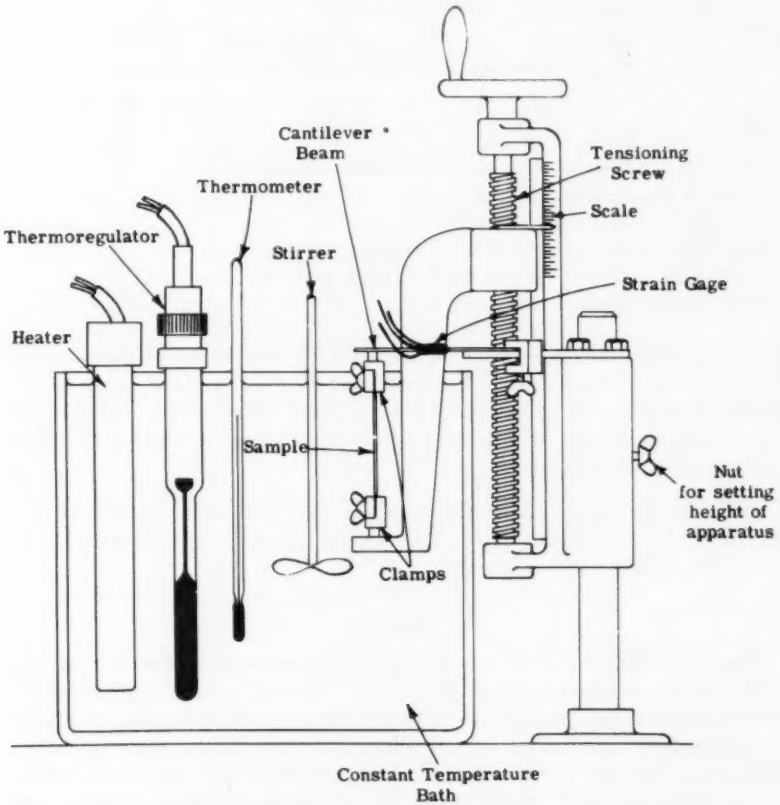

Figure I - Diagram of Apparatus

7. After completion of the stress-strain measurements the sample was carefully sliced at the clamp faces, blotted lightly with filter paper and placed in a stoppered weighing bottle. An average value for wet density of the tanned

tendon had been determined separately by weighing tanned KTT immersed in water at the stress-strain measurement temperature. From the wet weight, dry weight length, and density it was possible to calculate the average area of the tendon and the volume fraction of protein in the swollen KTT.

(1) $A = \frac{W_w}{d_w L}$

W_w = wet weight
d_w = wet density
L = wet length
A = average cross sectional area of swollen KTT sample.

(2) $v_t = \frac{d_s W_d}{W_w d_{dt} + W_d(d_s - d_{dt})}$. or $v_t = \frac{d_w}{d_s}(1 - \frac{W}{W_w})$

v_t = volume fraction of protein in swollen KTT.
d_s = density of solvent.
W_d = dry weight of KTT sample.
W_w = wet weight of KTT sample.
d_{dt} = density of dry KTT (Taken as 1.33)*.
d_w = density of wet KTT.

8. Chromium determinations on tanned KTT were made by digesting the samples, first with a mixture of concentrated HNO_3 and H_2SO_4 taken to SO_3 fumes, then with 70 per cent $HClO_4$ until clear. After cooling, and diluting to volume an aliquot was titrated iodometrically as chromate with starch as the end-point indicator.

9. Shrinkage temperature measurements were performed using a device, developed by M. Maeser in our laboratories, giving values in accord with A.L.C.A. requirements.

Results

The data obtained from stress-strain measurements, chromium analyses and auxiliary determinations of density and volume fraction are most readily considered in tabular and graphical form. Since the stress-strain studies give a quantitative estimate of the crosslinking process during tanning, the relationships between the number of added crosslinks and the more conventional properties such as shrinkage temperatures, chromium content, and basicities (as pH) have been treated in some detail. In addition, calculations based on the concept of active crosslinking sites (ionized carboxyl groups) have been included for comparison between experiment and theory.

The over-all reproducibility of the stress-strain data is ±5 per cent; the precision of the chromium analyses is within ±0.5 per cent, that of the cross-

*The density of dry collagen has been given by various authors as ranging from 1.50 to 1.41.

sectional area and volume fraction estimates within ±5 per cent, the pH measurements are within ±.01 pH unit, the shrinkage temperatures within ±0.2 °C.

Discussion

One of the concepts underlying our effort to develop an understanding of the chrome tanning process is that a major part of the process involves a

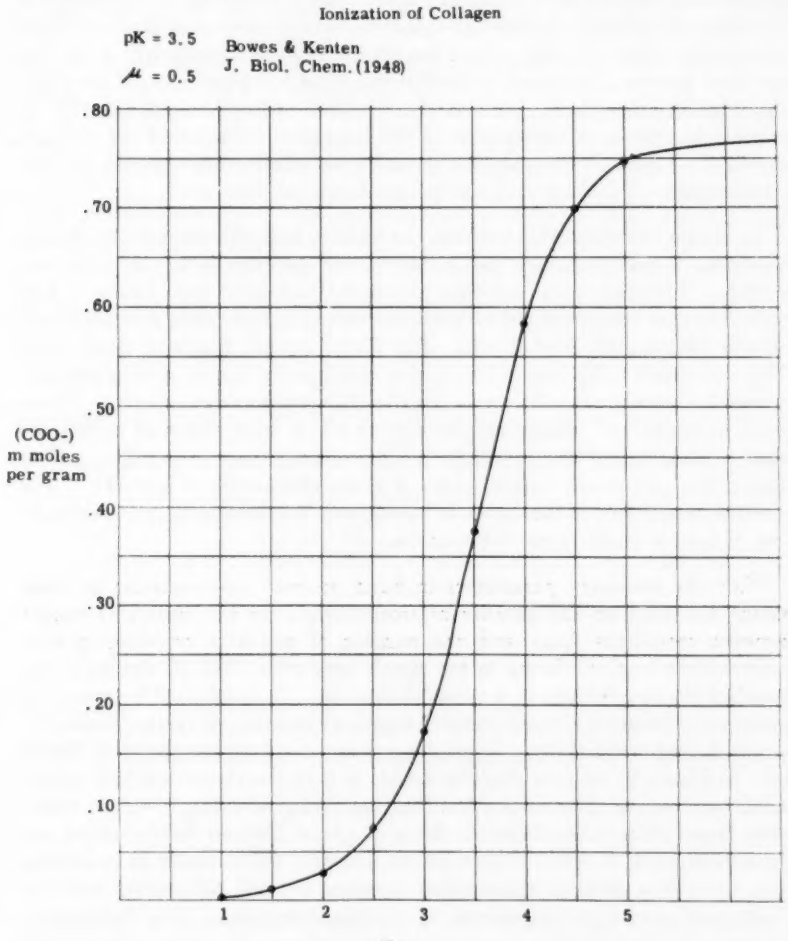

FIGURE IV

crosslinking mechanism. The basic reaction is believed to be that between a cationic chrome complex and an ionized carboxyl group of the collagen. In such a reaction the initial driving force is the electrostatic interaction, but as the reactants approach closely, the Werner-Pfeiffer type of bond becomes possible and a strong coordination link is formed that is thermally stable and is not readily reversible except in the presence of a high concentration of either hydroxyl or a competitive carboxylate group. With such a proposed crosslinking mechanism it becomes evident that a knowledge of the extent of ionization of collagen carboxyl groups under the conditions of tanning would be of great value. Further, if one has determined the average pK of the free carboxyl groups of collagen, it is then important to know the pH at which the reaction takes place. Fortunately, the work of Bowes & Kenten[5b]) on calfskin has given us an estimate of the ionization behavior of the collagen carboxyl. Figure IV presents the quantitative relationship between pH and concentration of ionized carboxyl groups based on their work.

To obtain the relaionship between the basicity and pH values of our chrome solutions, it was necessary to equilibrate the solution at 22–23 °C for one month. Previous work by Oppenheimer[16], Riess[17], and Jander[18] had indicated that the initial pH of basicified tervalent chromium solutions were always considerably higher than that found several hours or days later. This was found to be true in our case as well but the length of time required to reach constant pH values was considerably greater than expected. There were a number of interesting phenomena which were observed during the equilibration period and it is expected to consider them in detail at a later date. The pH versus basicity data is given graphically (Figure II). The unusual appearance of the curve, in having two intersecting slopes, is the subject of further study in our laboratories.

With the necessary parameters in hand we may now consider to what extent our data on the number of crosslinks (v_c) or the molecular weight between cross-links (M_c) and the number of available crosslinking sites (carboxylate ions) conforms to the simple prediction that all available carboxylate ions participate in a crosslink reaction. It is assumed here that an excess of crosslinking chrome complex is present and that no further ionization occurs during crosslinking. Typical stress-strain curves are shown in Figure III. In Figure V, we note that the shapes of both the theoretical and experimental curves are quite similar but that the predicted values of v_c are somewhat larger than those obtained. In spite of the obvious limitations of our theoretical basis, it seems reasonable to interpret these results as indicating that there is a definite relationship between the pH of tanning and the number of cross links introduced as chrome complexes. The discrepancy between the theoretical and experimental curves may be taken to mean that not all ionized carboxyl groups are available for crosslinking although the

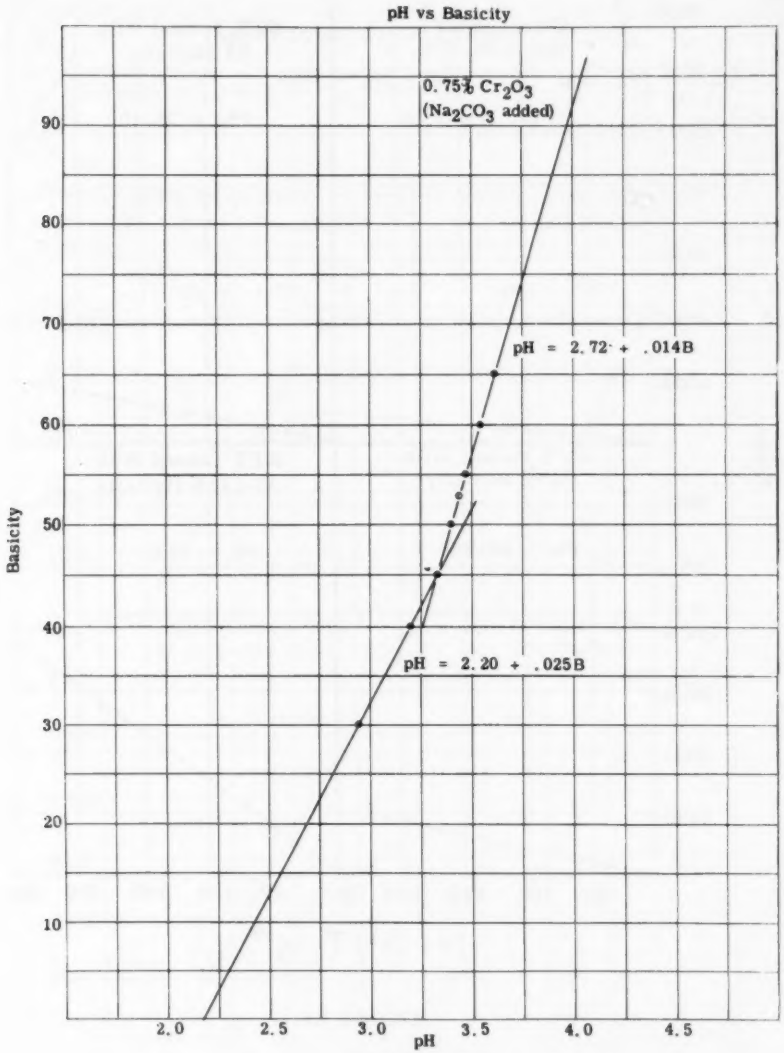

FIGURE II

assumption of no additional ionization during crosslinking has not been experimentally validated. This, therefore, leaves open the question of just what fraction of the ionized carboxyl groups is able to participate in the reaction.

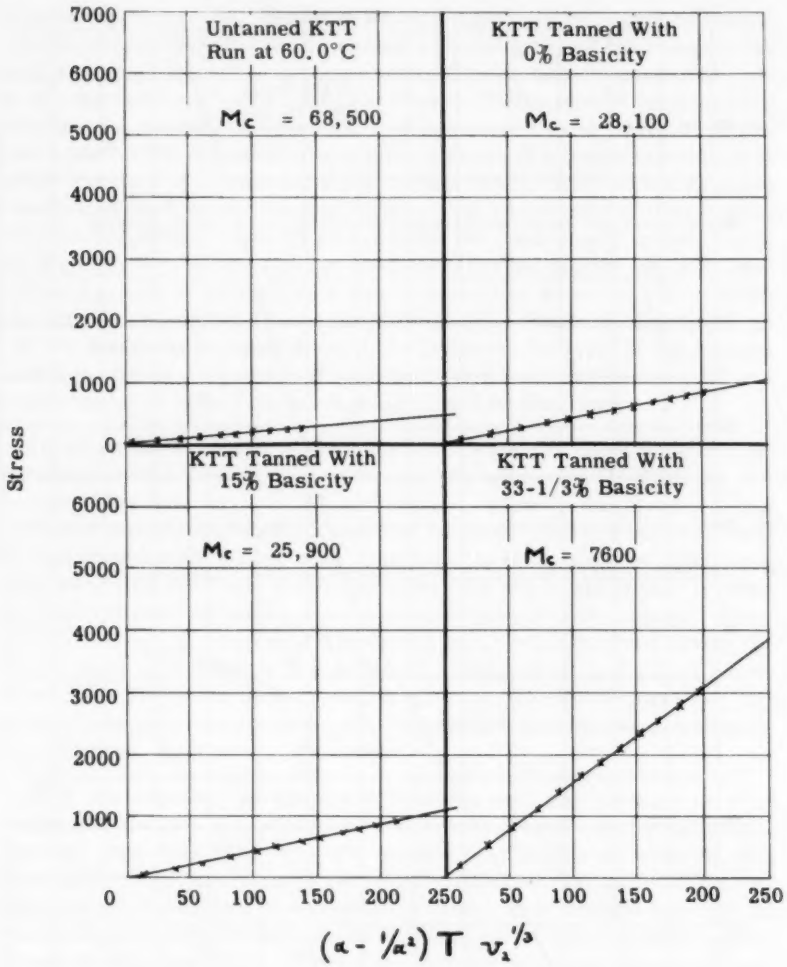

FIGURE III

It is, of course, implicit in our discussion that a crosslink, to be effective in our system, must link two chains and therefore two carboxylate groups, so that the steric restrictions operating against crosslinking may be formidable. A further point which requires some explanation is the behavior shown at the highest pH (77 per cent basicity). The decrease in v_c rather than the

Typical Stress-Strain Curves

Calculations: $S = \frac{RP\,(\alpha - 1/\alpha^2)\,T\,v_2^{1/3}}{M_c}$ $\qquad RP = 11.4 \times 10^4$

$$M_c = \frac{11.4 \times 10^4}{\text{Slope}}$$

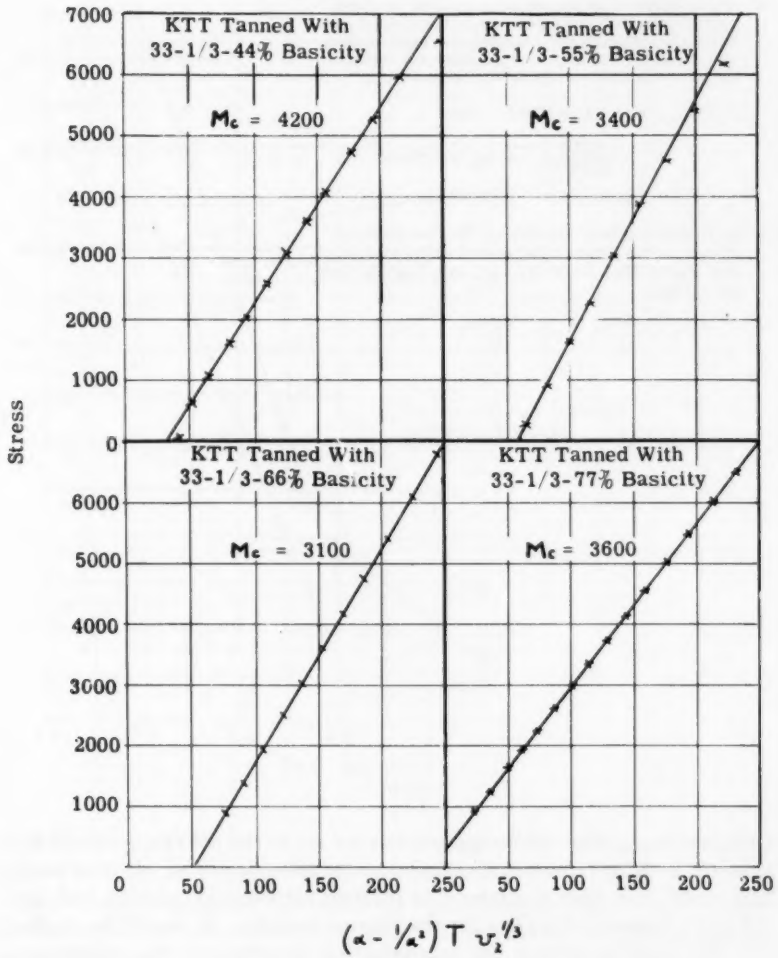

FIGURE III a

Degree of Cross Linking ν_c Versus pH

(1) The listed pH values are equilibrium values, in the tanning liquors used somewhat higher pH values existed at the listed basicities.

(2) ν is calculated as the maximum number of added crosslinks equal to the total number of ionized carboxyl groups per chain assuming that each carboxylate group participates in a crosslink and that no further ionization occurs during the process.

$$\nu_c \text{ (max)} = \# \text{ of } (COO)^-/\text{chain}$$

$$= \frac{(COO)^-}{(COOH)} \times M_o \times (COOH)$$

$$= \text{moles } (COO)^- \times 68,500$$

(3) M_c is obtained from the slope of the line obtained by plotting the stress as a function of the extension (see Figure III). From M_c, ν_c is calculated from the relation

$$\nu_c = \frac{M_o}{M_c} \qquad 1 = \frac{68,500}{M_c} - 1$$

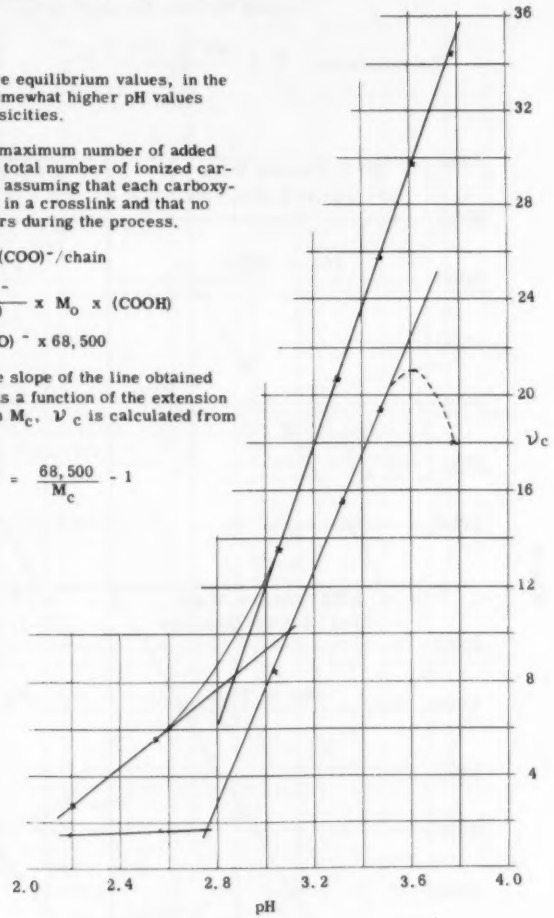

FIGURE V

predicted increase in value suggests that we are in the pH range in which a sufficient hydroxyl concentration exists to permit a detanning effect to occur. This could arise from a competitive reaction between the solution hydroxyl and the collagen carboxylate for the chrome complex. It should be recalled that the actual tanning is not an equilibrium process and that sodium carbonate is added at intervals until the final basicity is reached. The possibility of crosslinks that have been formed at lower pH values (basicities)

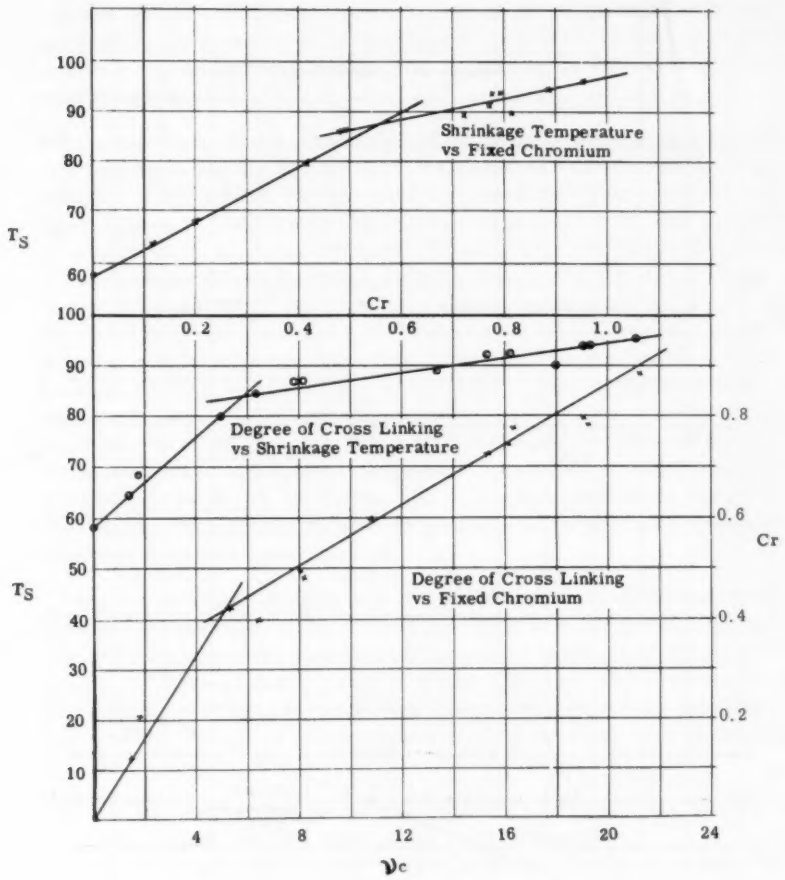

FIGURE VI

then being, in effect, destroyed by the appearance of additional hydroxyl groups seems to be a reasonable interpretation.

The factors responsible for conferring hydrothermal stability on chrome tanned leather are still a matter of debate. The unclear status of the shrinkage process and the lack of data on the relative extent of inter-chain and intra-chain binding by chrome complexes contribute to the uncertainties surrounding the relation between the shrinkage temperature and extent of tanning.

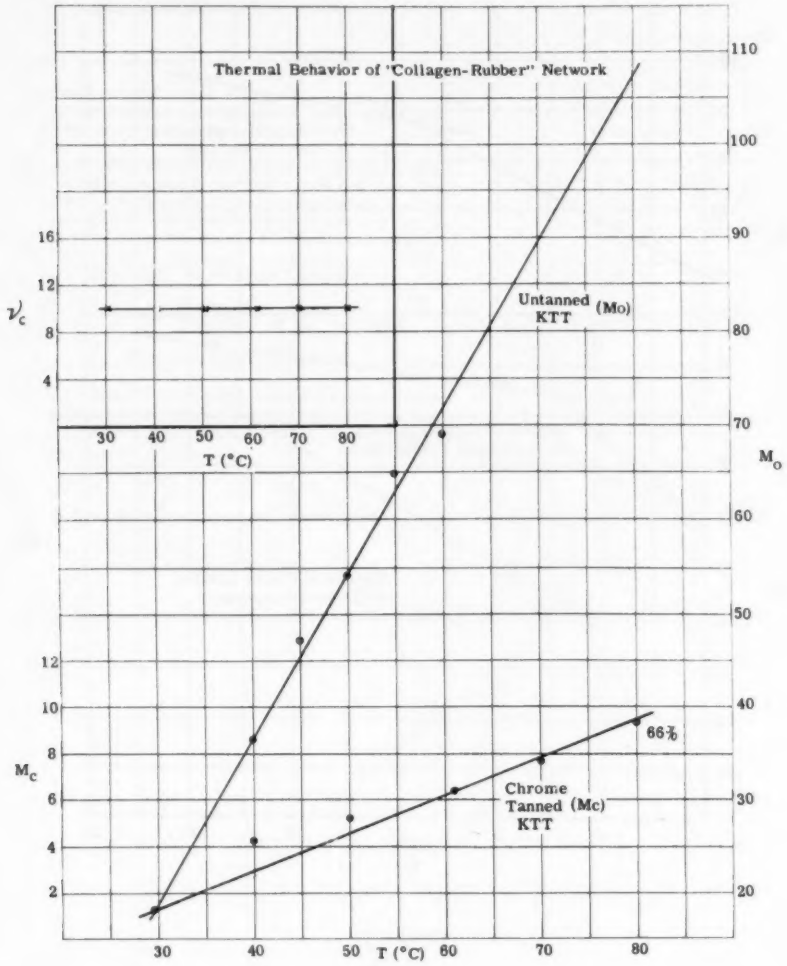

FIGURE VII

It is obvious from Figure VI that no simple relationship exists between the shrinkage temperature (T_s), the number of added crosslinks (v_c) and the extent of chrome bound to the collagen millimoles/gm. collagen (Cr). The characteristic break in the linear plots which pervades all our data reinforces the concept that at least two basic mechanisms are operative during chrome-tanning. One mechanism, that of bifunctional inter-chain crosslinking,

appears to operate throughout the range of the experiments; the second mechanism, more obscure in nature, appears to govern the binding of chromium in a non-crosslinking fashion and appears to be limited to the higher basicity region.

Previous results in this laboratory had led to the hypothesis that a covalent link between rubbery polypeptide chains existed in hydrothermally shrunken collagen. The marked improvement in sensitivity of our modified stress-strain apparatus now permits the detection of changes in M_c due to changes in the temperature of measurement. Figure VII presents the temperature of the "collagen-rubber" network for both untanned KTT and KTT tanned at a final basicity of 66 per cent. The results on untanned KTT cannot be reconciled with the presence of a covalent crosslink. The considerable decrease in temperature dependence of M_c for the chrome-tanned KTT is to be expected from our knowledge of the stability of a chromium-carboxylate coordinate bond. However, the calculation of v_c (the number of added crosslinks) from M_o (from untanned KTT data) and M_c (from tanned KTT data) reveals the unsuspected result that v_c is constant with measurement temperature as shown in Figure VII. The combination of temperature dependent molecular weights between crosslinks and temperature independent crosslinks requires a new hypothesis.

Here we introduce the idea that the shrunken untanned collagen network is formed by thermally stable crystallites acting as giant crosslinking regions. The crystallites become smaller with increasing temperature by removal of polypeptide chains laterally or by shrinkage linearly. (This process may also be brought about by solvents having high swelling power for proteins.) In this way the fraction of rubbery material (M_c) increases with temperature. The results after tanning may be interpreted in two ways:

1. (a) Chrome-tanning introduces crosslinks of very high thermal stability outside the thermally stable crystallite regions.
   (b) The crystallite network retains substantially the same behavior as in untanned tendon.
   (c) The temperature dependence of the tanned KTT is the resultant of the stable chrome crosslinked network and the less stable crystallite network. (The ratio of M_o at T_1 to M_o at T_2 is close to that for M_c at T_1 to M_c at T_2, i. e., about 1 crosslink broken, both in tanned and untanned KTT, for a 10°C. rise in temperature.)

2. (a) Chrome tanning introduces crosslinks throughout the collagen structure.

   (b) The chrome cross-linked crystallites have a much higher thermal stability.

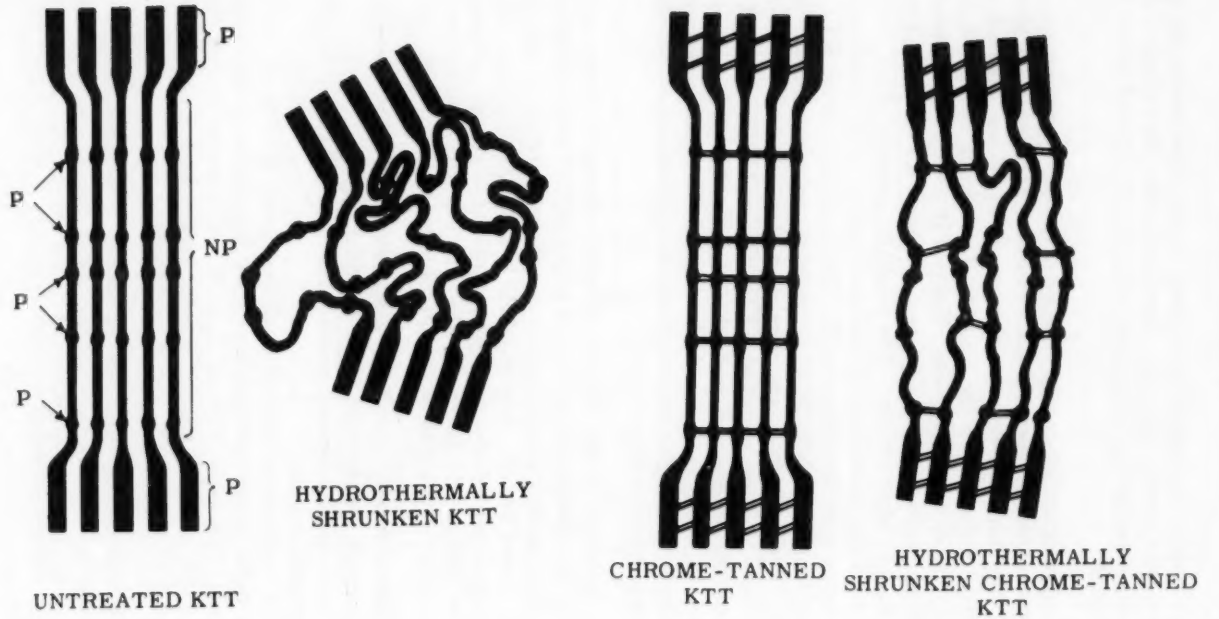
P
P
NP
P
P
P
UNTREATED KTT
HYDROTHERMALLY SHRUNKEN KTT
CHROME-TANNED KTT
HYDROTHERMALLY SHRUNKEN CHROME-TANNED KTT

FIGURE VIII

(c) The lower temperature dependence of the tanned KTT is the result of the higher proportion of polypeptide chains incorporated into the network crystallites due to the chrome crosslinking.

(d) The number of crosslinks added by tanning remains constant with varying temperature because the crosslinks are crystallites which can become smaller in size as the temperature increases but will remain constant in *number*.

In order to illustrate the structure and mechanisms discussed above a diagrammatic sketch is given in Figure VIII. Other methods, independent of the stress-strain technique, are to be employed in evaluating the crystallite network hypothesis and are now in progress.

Summary

The stress-strain behavior of hydrothermally contracted chrome tanned tendon collagen has been investigated. The data have been treated in terms of the kinetic theory of rubber elasticity. The major conclusions reached in the course of this work are:

1. The number of crosslinks introduced by chrome tannage is closely related to the pH (basicity) of the tanning solution and its effect on collagen carboxyl ionization and chrome complex composition.

2. The relationships between shrinkage temperature and fixed chromium on the one hand and the degree of crosslinking and pH of tanning on the other have been demonstrated.

3. The process of chrome tanning involves two major mechanisms (1) crosslinking and (2) nonspecific binding, which are related to the change in properties of the chrome liquor above a critical basicity range.

4. Analysis of the temperature dependent behavior of the "collagen-rubber" network, both untanned and tanned, has led to a new structural hypothesis. It is now believed that hydrothermally shrunken collagen is a network based on thermally stable crystallites acting as giant crosslinks between amorphous polypeptide chains.

Acknowledgment

The authors wish to acknowledge the many stimulating and helpful discussions with Dr. J. H. Highberger and Dr. Shu-Tung-Tu.

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Discussion

Dr. Turley: (Rohm and Haas Company) Fellow members, this paper certainly conforms to the expressed wish of President Flinn that we have new approaches to leather research and new methods, so that ultimately we can explain some of our age-old basic methods of making leather.

The chrome tanning process of course lends itself rather than the vegetable process, to different kinds of studies, because of the temperature resistant nature of chrome tanning.

I can only say that I think possibly the Program Committee asked me to lead this discussion because I might give a little different point of view, as I know nothing about this type of work and I know very little about the literature.

However, if we reflect back we know the origins of this thinking about chrome leather. In a meeting like this, we can go back to John Arthur Wilson conjecturing on the cationic nature of chrome tanning, and much has been added since then.

These new physical mathematical approaches are probably destined to give us a better understanding of the crosslinking of the protein and what it takes to make a satisfactorily tanned leather.

The experimental conditions here, I think we should point out, are not to be translated directly or too directly, at least yet, to chrome tanning, regardless of the fact that they are done on the tendon of the kangaroo tail and that might be quite a big jump over to cowhide.

I think Dr. Naidus has pointed out what we have all realized, the very great difference between his experience on isolated fibers and the experiments, which possibly the practical men are more interested in, dealing with the hide structure. We not only have the fibers but this very wonderful network of fibers.

I think Dr. Naidus has two interesting points—they are: to point out the question of the crystallinity of the areas of collagen fibers. Dr. Philips touched on that. I forget whether it was here or in the meeting of the International union. It is relatively new coming around to the idea that, while there are collagen fibers of large amorphous areas, there are also crystalline areas. When you describe the leathermaking treatment—liming, bating and pickling, it leaves open a tremendous area of research.

Then there is this most interesting area of the non-crosslinking chromium. One wonders whether there would be differences if these tendons were treated in such a way that they are perhaps no longer bundles but are broken up into these individual fibrils, and what would be the differences there?

Also, what might be the effects in a simple classical tannage of chrome, namely, the treatment first of all with the bichromate, subsequently reduced and actually producing chrome leather—whether we would get different interesting pictures of this non-breaking chrome.

Then what about some of the new ideas in solvent tannage, where we are not perhaps dealing with ionized systems, but may be producing chrome leather possibly of an entirely different type? The amount of crosslinking may be considerably reduced or otherwise.

I believe in this field there are relatively few workers but I would like to ask if anybody has any contribution to make, or any questions to ask, say, from the Bureau of Standards group which has done work along parallel lines. Is anybody here from the Bureau of Standards who would be willing to add to this discussion?

DR. J. R. KANAGY (National Bureau of Standards): I would like to ask Mr. Naidus one question: has he made any calculations as to the concentration of these crosslinks? That is, in the amount of millimoles per gram of collagen or what the concentration of them could be?

MR. NADIUS: In the slide which showed the temperature constancy of the number of crosslinks, they ran around twelve crosslinks added per untanned network chain. One has to remember that the crosslinks which are put in by chrome tanning are added to an already crosslinked structure. To know that initial crosslinking one would have to assign some value to the primary unit.

We have made some preliminary calculations along that line in which we have assumed that the primary unit is about 300,000 in molecular weight. And we believe that the ordinary, untanned tendon, when it is shrunk—and mind you it is only valid for the shrunken mateial—when it is shrunken it has approximately five or six crosslinks per primary chain.

Now, what we do when we chrome tan is to form in addition to the five or six original crosslinks approximately ten to twelve new crosslinks. And it can be even higher. Of course it depends on the particular point at which you stop—you will get either greater or lesser numbers of crosslinks.

KANAGY: You assume possibly that the crosslinks are between two carboxyl groups?

NAIDUS: Yes.

KANAGY: Since you know the concentrations of carboxyl groups in the molecule, you could tell the proportion of those groups which had reacted.

NAIDUS: The earlier slide showing a theoretical curve, which was based on just such a calculation, indicated that not all the ionized carboxyl groups were actually participating, although the close parallelism of the two curves led us to believe there was, in fact, a direct relationship.

I do not think that in a structure as complex as a protein, with the obvious steric problems which are quite formidable, one could expect that every ionized carboxyl group would be in a sterically favorable situation. On the other hand it is important to remember that only ionized carboxyl groups

seem to participate and one should distinguish between the carboxyl groups present in the uncharged form and those present in the charged form. It is likely, since we are dealing with the cationic chrome complexes, that they will be oriented to charged carboxyl groups—that you will have a positively charged complex and a negatively charged carboxyl ion. And the impetus fort he carboxyl-complex bond is an electro-static one and, if one operates under pH conditions that favor this situation, one should get maximum crosslinking if that is what is desired under those conditions.

DR. LOLLAR: (Tanners' Council Research Laboratory) One question in this line: I believe these were unlimed kangaroo tail tendons?

NAIDUS: Yes.

LOLLAR: So that there would be a reduction of free carboxyl groups and therefore a reduction in crosslinking?

NAIDUS: We have done some experiments which indicated that liming did in fact release the amide side-chain carboxylate groups, but if they were included in the calculations substantially the same results would be reached.

We modified our calculations to exclude those carboxyl groups that were not free, because we had not limed. But where we used limed tendons and followed the conventional practice of carrying the tendons through the usual tanner's preparation for tanning, we discovered substantially the same conclusions would hold—that you released more carboxyl groups by liming and therefore we expect to get more crosslinking at a given pH.

DR. STUBBINGS: (Lehigh University) It is interesting to note that we have just completed some work at Lehigh on the problem of shrinkage reactions based on entirely different techniques, namely measurement of calorimetric heat contents, and in order to correlate the data we found it necessary to postulate crystalline sections or portions of the molecule.

This was the only way we could make the data come out reasonably well. We also found we had to postulate a sort of fusion as part of that process. We think of it as an internal fusion of those chains and apparently your results indicate exactly the same thing.

So I think maybe we are heading at least in the same direction.

I have one question, however: when you showed your data that indicated that you got two different effects from chromium with pH, plotting pH versus basicity, did you consider the possibility that in a straight chrome sulphate liquor when you get to the basicity you indicated on the second portion of your curve, that you probably have considerable precipitation?

NAIDUS: That was generally true.

STUBBINGS: Wouldn't you say that precipitated chrome would behave differently than cationic chrome?

NADIUS: The interpretation we gave was that above the critical pH region you actually observe precipitation to occur unless there are carboxylic acids such as tartaric or those from glucose present.

Our understanding there is that, yes, this is true—that solid materials are precipitated but this only reinforces the conclusion that something different happens above this pH region to cause complexes to grow to such size that they actually precipitate and the indications are that a new process has set in, in going beyond this pH range. However, the basicity pH relationship is based on the soluble material only.

So that the fact that some of the material has precipitated out merely indicates visibly what the pH measurement already shows—that a new relationship between pH and basicity has been established above this region.

STUBBINGS: I do not understand your line of argument but the simple explanation is that the chromium precipitates inside the fiber or outside, depending on where it is at the moment, and possibly you would expect less effect from that chromium from the standpoint of shrinkage increase. It looks as simple as that.

I would like to look the data over more carefully, but it seems to me a very straightforward interpretation that the chromium that is precipitated is not acting as crosslinking chromium.

NADIUS: I am sorry, I was answering the comment on pH and basicity. Yes, it is true that material just precipitated is likely to be calculated as fixed chrome, but would have no essential effect on the material other than added weight.

STUBBINGS: Along the same line then, I assume your data showing shrinkage temperature versus the chromium bound, was taken purely from the experiment where you continually increase the basicity of the chrome liquors?

NAIDUS: Yes.

STUBBINGS: What is the effect if you increase the chromium content at the same pH conditions by increasing the concentration of the cationic chrome?

NADIUS: We have not done that experiment. It is one of the lines of work we are following—the general problem of equilibrium conditions as compared with the conventional tanner's situation where he is working with non-equilibrium conditions.

We recognize this as a difficulty of any interpretation of the chrome tanning process, unless one isolates the factors and puts them under equilibrium conditions.

STUBBINGS: We could take either tanner's or equilibrium conditions from the amount of chromium bound by simply increasing the concentration of chromium in solution. There you can talk of one hour reaction or equilibrium. I do not think it has a bearing on the problem. But the question is, would you get the break in slope with increased chrome content if you put the chrome in under such conditions that the pH was constant? It seems to me the data showing the break in shrink temperature with increased chrome content is apt to be misleading in the sense that it was taken only by the particular experimental conditions you used where you put chromium on under conditions where it was precipitating. If you had done so under conditions where it was not precipitating, I think you would have gotten a straight line function or a function that did not show a break of that type.

NADIUS: I was merely trying to develop the idea that under the conditions we used there seemed to be two main processes at work. I grant you that anything you do which permits more chromium to stay in solution is likely to find more chromium combined with collagen.

There seems to be no inherent limit to the amount of chrome you can combine with collagen. There is a limit to the amount of chrome you can cross link with collagen, because there are only a certain number of sites that will yield crosslinks. You can combine along the polypeptide chain with any amount of chrome you can get in, in soluble form. I grant when you add a complexing or masking agent you are likely to improve the amount of chrome bound and therefore you will shift this break to higher shrink temperature and higher chrome concentrations, but I believe, however, that eventually if you reach a precipitation point you will find that characteristic of a fall in slope.

STUBBINGS: I raise the issue because we published data sometime back showing the result of increase of chromium concentration on fiber shrinkage, and those curves show no such double break as your curves. They showed a simple increase that slowly dropped off with decreasing amounts of chrome, as if it were acting as a homogeneous system; and I think the break is due entirely to precipitation and has nothing to do particularly with increasing just the chrome concentration.

TURLEY: There might be a point there in the way the work was done—to give 33 per cent basic chrome and after the tannage had been running for sometime adding sodium carbonate. It is appreciated in the chrome leather industry that you get different results if you tan at a lower basicity.

Is there anybody from M. I. T. here who would like to add to the discussion? If not, I will retire in favor of my colleague, Dr. Merrill.

DR. MERRILL: (B. D. Eisendrath Tanning Company) I do not think I can add much to the discussion that has already taken place. On the matter

of the question of pH versus basicity in the equilibrated solutions, it would be very interesting to see what results you got if you had raised the basicity not by using sodium carbonate but sodium hydroxide inasmuch as some cabonato complexes are formed at higher basicity.

I would also point out that all of these measurements were made on leather which had been raised to a much higher basicity than the basicities indicated, because the tanned tendons were washed twenty-four hours in running tap water, which would probably have accomplished almost complete neutralization.

I discussed that with Mr. Naidus before the meeting and he feels that after the tanning has taken place, no further crosslinking can take place as a result of neutralization. I think that is something that would have to be proved.

As to the detanning at the higher pH values, I discussed that with Mr. Naidus too, and he does not mean by detanning what we ordinarily mean—the actual removing of the tanning agent, but really a change in the manner in which it is combined, probably by replacement of carboxyl linkages by hydroxyl groups.

I think Mr. Naidus is much to be congratulated not only on the work he has done, but on the way in which he has presented a very difficult subject.

ABSTRACTS

Tanning Material Developments. *The Leather World*, **47**, No. 27, 503 (1955). Based on a report from the Forestal Land, Timber and Railways Co. Ltd. the impression is conveyed that tanners have little need of anxiety concerning the supply of vegetable tannin in spite of a substantial decline in the production of Quebracho and the indication that the decline will continue. Part of the apparent reduction is due to the stockpiling of 22,000 tons of Quebracho by the United States during 1953. There has been an increase of Wattle production which, while not enough to offset the reduction in Quebracho, continues to increase as the Quebracho decreases. Figures substantiating these conclusions are given in the following table.

Exports of Wattle and Quebracho Extracts from Producing Countries

	1951	1952	1953	1954
			1,000 tons	
Argentina	256.4	171.5	183.1	153.0
South Africa	83.9	92.8	95.5	95.0
Kenya	22.2	24.0	22.1	24.2
Total	362.5	288.3	300.7	272.2

Distribution of Quebracho exports from Argentina is as shown in the next table.

Exports of Quebracho Extract from Argentina

	1951	1952	1953	1954
		1,000 tons		
United States	123.7	98.0	96.7	60.2
United Kingdom	25.2	3.7	8.5	6.6
West Europe	53.2	35.0	35.7	34.9
East Europe	12.2	11.0	5.9	14.8
South America	11.6	14.6	14.2	16.3
Rest of World	30.5	9.2	22.1	20.2
Total	256.4	171.5	183.1	153.0

There has also been a continued increase in the use of synthetic tannins as may be seen from the data given in the following table.

Export of Synthetic Tanning Materials from Western Germany

	1951	1952	1953	1954
		Metric Tons		
Belgium	112	202	324	405
Denmark	83	78	149	189
Finland	223	131	92	288
France	293	174	150	157
United Kingdom	42	121	171	216
Italy	167	295	432	560
Holland	351	541	659	734
Norway	74	93	238	224
Austria	314	166	183	278
Sweden	46	57	188	249
Switzerland	143	100	181	301
India	3	16	—	122
Mexico	80	103	107	194
Chile	15	107	64	107
Colombia	90	484	487	816
Peru	77	103	54	37
Uruguay	65	—	100	108
Venezuela	39	289	435	155
All Countries	3,342	3,697	4,801	6,076

The use of vegetable tannins outside the leather industry (as in boiler feed water and drilling mud control) is also on the increase. It will be a long time before it attains the dimensions of the use in tanning. R.H.T.

Note on Leather Analysis. By G. Forsyth. *J. Soc. Leather Trades' Chemists,* **39,** 105 (1955). Ground leather powder prepared with a Wiley mill and leather shavings cut according to the Official Method of the Society of Leather Trades' Chemists are shown to analyze for the same moisture content. Comparative water-soluble analyses using the Reed-Churchill extraction of ground leather at 35°C. and the Official Method extracting shavings

at 45° C. show that the former can give results up to 5 per cent greater than the latter. The Procter extractor is not suitable for use with ground leather, the extraction being irregular. Ground leather analyzed for water solubles by the Swiss Leather Chemists' Society Method had a slightly higher value than that obtained on leather shavings by the British Society method. J.M.C.

The Accessibility of the Cationic Groups of Collagen to Large Anions of Polybasic Acids. By A. Larsson and K. H. Gustavson. *J. Soc. Leather Trades' Chemists*, **39,** 107 (1955). The interaction of protons from polybasic acids with carboxyl ions of collagen does not alter the heat content of the system; whereas the discharge of the cationic groups of collagen, by hydroxyl ions or by electroneutralization through fixation of the anion, results in heats of reaction of the order of 10-14 kcal. per mole. Using this fact, measurement of the number of ionic sites of a polyvalent anion which are able to discharge the cationic groups of collagen is possible. From the titration curves, obtained upon interaction at 10°, 20°, and 30° C., respectively, of hydrochloric acid and lignosulfonic acid (avg. mol. wt. 5-6,000) with collagen and with collagen lightly tanned with formaldehyde, the values of $-\triangle H$ were obtained by means of Clapeyron's equation. This value for hydrochloric acid is 1-2 kcal. per mole as compared with a value 6-7 for lignosulfonic acid, indicating that about half the cationic groups of collagen are irreversibly inactivated by fixation of lignosulfonic acid. The same conclusion is reached by reacting methylated collagen with lignosulfonic acid and determining the exchange of chloride bound anions of the methylated sample for lignosulfonic acid anions J.M.C.

Study of the Kinetics of Olation. By S. G. Shuttleworth. *J. Soc. Trades' Chemists*, **39,** 105 (1955). Olation of chrome liquors rendered basic proceeds according to the following stepwise pattern: (a) aggregation due to hydrogen bonds (rapid); (b) mono-ol. formation (slow); (c) di-ol. formation (rapid); and (d) tri-ol. formation (rapid). The phenomenon of olation is attributed to the formation of stable resonant rings involving an OH joining two chromium atoms. Hexaquo chromium salts, having to pass through step (b) above, olate slowly. The rate of de-olation of an olated complex by acid is very slow at room temperature. Complexes having multiple rings de-olate less slowly than those with single rings. Standard reaction velocity equations apparently do not fit the results obtained. A technique used in determining degree of olation should take account of the very slow effect of excess acid compared with the very rapid reaction of alkali on a partially olated complex. Tanning methods should be planned to take account of the high rate of irreversible absorption of added alkali by the chrome tanning liquor and nonavailability of this olated OH for neutralizing free acid without a considerable time factor. J.M.C.

PATENTS

Process for Preventing the Fulling Shrinkage of Wool. U. S. Pat. 2,714,051. Charles R. Barnes, Pittsburgh, Pa., assignor to Albany Felt Company, Albany, N. Y., a corporation of New York. Apl. April 15, 1949. 1. The method of preventing the fulling shrinkage of wool by treating it in a water solution of three substances comprising an acid, and a metal bromate and a metal bromide capable of yielding in said water solution bromic and hydrobromic acid, respectively, when combined with said acid; said method comprising, first immersing the wool in a water solution of any two of said substances, and thereafter forming nascent bromine in said solution by adding said third substance thereto at a com-

paratively slow rate and less than that which will effect a substantial brownish discoloration of said solution; whereby to effect the formation of said nascent bromine in said solution at a rate approximating the rate it reacts with the wool and to prevent formation of free molecular bromine in said solution; said bromate and said bromide being used in stoichiometrical amounts producing nascent bromine in a total quantity constituting from about 1% to about 5%, by weight, of the wool.

Beta-Propiolactone Modification of Wool. U. S. Pat. 2,717,194. William Gordon Rose and Harold P. Lundgren, Berkeley Calif., assignors to the United States of America as represented by the Secretary of Agriculture. Apl. October 21, 1954. (Granted under Title 35, U. S. Code (1952), sec. 266). 1. A process for chemically modifying wool comprising reacting wool with beta-propiolactone in the presence of a liquid medium at least 10% of which is a high-molecular weight aliphatic alcohol containing at least 8 carbon atoms.

Process for Degreasing Wool and the Recovery of Wool Grease. U. S. Pat. 2,717,901. Daniel P. Norman, Ipswich, Mass., assignor to Pacific Mills, Lawrence, Mass., a corporation of Massachusetts. Apl. January 31, 1951. 1. The process for the recovery of wool grease from raw wool which comprises leaching the raw wool with tetrachlorethylene to extract wool grease therefrom, separating the liquid extract from the wool fibers, dividing the liquid extract without addition of other material thereto, by treatment consisting of separation by difference in specific gravity, into a portion rich in wool grease and a portion rich in tetrachlorethylene, and separating the portion rich in wool grease from the other portion.

Blades for Skin-Treating Machines. Brit Pat. 707,891. Tanners Research Corporation. Apl. Feb. 20, 1951. A blade adapted to be secured in helical formation in a cylinder of a skin-treating device is formed from a strip of material softer than the working edge and has a layer of chromium attached to and restricted to an outer end portion of the blade; the outer end is of planar form substantially at right angles to the strip in the case of a cutting blade, or of rounded form in the case of a scraping blade. The cutting blade may be made of soft steel and may have an insert of hard steel in the outer end portion of the leading face. The scraping blade may be made of stainless steel, brass or bronze and the outer end portion of the leading face may be backwardly bevelled. The chromium may be applied to a thickness of 0.003-0.006 inch by plating before or after mounting the blades in the cylinder. Thc bladed cylinders are used in fleshing, unhairing, and setting-out machines. Specification 629,845 is referred to.

Making Leather. Brit. Pat. 720,505. Verband Der Deutschen Lederindustrie. Apl. May 14, 1952. Hides and skins are preserved by impregnating with an ester, ether, carboxylic acid, carboxylic acid anhydride or an ethylenic hydrocarbon which has ethylenic unsaturation and is capable of vinylpolymerization together with a copolymerizable substance if desired, and simultaneously or subsequently polymerizing within the hide or skin. Polymerizable and co-polymerizable substances specified are: vinyl acetate, ethyl vinyl ether, decahydro-β-naphthol vinyl ether, butadiene, styrol, acrylic acid, methacrylic acid, crotonic acid, maleic acid, maleic anhydride, oleic acid and allyl alcohol esters. The skin or hide may be filled with an aqueaus emulsion of the polymerizable substance. Emulsifiers specified are fatty alcohol sulphonates and sulphonated oils. Polymerization accelerators, e.g. benzoyl peroxide, ferrous salts and hydrogen peroxide may be employed. The process may be combined with known tanning processes.

Oil-proofing Leather &c. Brit. Pat. 721,482. Wilkins, Campbell & Co., Ltd. Apl. April 21, 1953. An oil-resistant washer is made of natural or artificial leather impregnated with a mixed ether of a phenol and a polyhydric alcohol, and, if desired, a wax. The ether may be made from glycol or pentaerythritol and a phenol or may be mono- or dicresyl glyceryl ether, while the wax may be hydrogenated caster oil.

Coated Paper, Leather, and Nylon Fabric. Brit. Pat. 722,774. Du Pont De Nemours & Co., E. I. Apl. Nov. 13, 1952. A dispersion which may be employed in the preparation of binders, for coating paper, for treating leather and the preparation of leather-like products comprises an aqueous dispersion containing (1) from 1 to 50 per cent based on the total weight of the dispersion of a N-alkoxymethyl polyhexamethylene adipamide, (2) a cationic, anionic or non-ionic dispersing agent, and (3) a water-soluble salt derived from a nitrogen-containing base and an acid having an ionisation constant for the first or only hydrogen of at least 1×10^{-5} at 25° C., said salt being decomposed on heating to a temperature of 170° C. to yield an acidic residue which effects curing of the modified polyamide. In an example a cowhide leather is sprayed with a mixture of 2 parts af an aqueous dispersion of N-methoxymethyl polyhexamethylene adipamide containing 13 per cent of the polyamide and a small quantity of sodium dodecyl sulphate and ammonium citrate and 1 part of a casein dispersion containing a red dye. After drying at 80° C., the coating is ironed at a surface temperature of 149° C. whereby the leather surface acquires a glossy finish. The Specification further states that the application of the dispersion as a binder to a fabric comprising nylon staple as the structural fibre plus cellulose acetate as the extractable pore-former, results in a leather-like product.

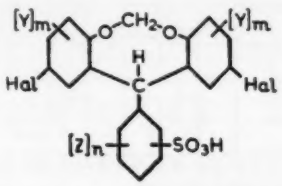
Treating Hides and Skins. Brit. Pat. 725,671. Fairweather, H. G. C. (General Dyestuff Corporation). Apl. Jan. 26, 1953. Hides, skins and leather are treated with a composition comprising water and a copolymer of a vinyl alkyl or alkyl substituted ether with maleic anhydride in which from about 5 to 15 per cent of the anhydride groups have been converted to the ammonium or substituted ammonium salt—half amide (*see* Group IV (a)). The copoiymers may be employed in conjunction with other tanning agent, e.g. alum or natural tanning. In the production of chrome leather the copolymer composition may be used either prior to tanning with chrome or applied on the shaved blue stock. The treated hides, skins and leather may be dyed subsequently. The hides, skins and leather treated may be chrome tanned calf, Nigerian skins, suede kid, goatskins or calf suedes or splits.

Treating Hides and Skins. Brit. Pat. 725,672. Fairweather, H. G. C. (General Dyestuff Corporation). Apl. Jan. 26, 1953. Hides and skins are treated in the presence of water with a vinyl alkyl or alkyl substituted ether-maleic anhydride copolymer (*see* Group IV (a)), preferably at a *p*H of about 2.5 to 4.0. The copolymers may be employed in conjunction with other tanning agents particularly those employed in chrome tanning. Hides and skins mentioned are goatskins, calf suedes and splits and suede kid stock. The *p*H may be adjusted by alkali metal hydroxides, ammonium hydroxide, carbonates or organic bases. The copolymers may be applied to the hides and skins before pickling or subsequently or before chrome tanning and preferably 0.5—6 per cent by weight of the polymer is incorporated into the hides and skins.

Shaping Prior to Tanning or Finishing Leather. Brit. Pat. 726,777. Secotan, Inc. Apl. Dec. 4, 1951. A process of forming hollow leather articles such as shoe uppers

directly from limed, dehaired and bated or pickled and untanned skins comprises clamping the margins of the blank and forcing the unconfined area of the blank by fluid pressure into conformity with a hollow porous mould. The pressure may be by suction or direct liquid pressure, in which case the liquid may be a dehydrating fluid such as acetone or alcohol. This may be followed by other treating liquids such as the tanning liquids, fat liquor and a dyeing liquid in any order. The surface of the mould may be such that it produces ornamentations or other markings on the grain side of the skin, and in shaping an upper a marginal flange or a bellows formation at the instep may be produced. The blank may be tensioned in any direction to cause the fibres to be oriented in any desired direction. A treated shoe upper may have a stiffening compound applied directly to the counter or toe portions while in the mould. For producing lined uppers, superposed plies of untanned skin may be employed and treated as a single blank. The apparatus used comprising the porous mould is described and claimed in Specification 726,828. Any watermiscible solvent may be used in place of acetone or alcohol. A chrome tanning solution or vegetable solution may be used or aldehyde, aluminium, titanium and zirconium tanning solutions. It is practical to combine the tanning and dehydrating solutions.

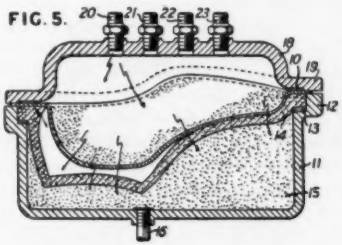
Mothproofing Keratinous Textile Materials. Brit. Pat. 726,789. Farbenfabriken Bayer Akt.-Ges. Apl. May 30, 1952. Keratinous textile materials are mothproofed by treatment with a compound of the formula



where Y and Z may be hydrogen, halogen, alkyl, alkoxy, amino or acylamino; n and m are integers and "Hal" represents a halogen atom (*see* Group IV (b)). In an example, a material is treated with the sodium salt of 2 : 2^1-methylenedioxy - 3 : 5 : 3^1 : 5^1 : 4^1 - pentachlorotriphenylmethane-2^{11}-sulphonic acid.

Shaping and Tanning Leather. Brit. Pat. 726,828. Secotan, Inc. Apl. Dec. 4, 1951. An apparatus for moulding and fluid-treating a skin more particularly in the production

FIG. 5.

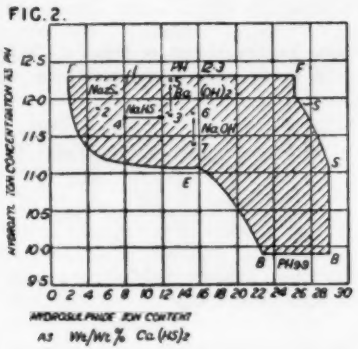


of a shoe upper comprises a hollow mould 14 of plaster of Paris or like porous material

supported on a bed of sand 15 and gasket 13 in a container 11 on to which a cover 18 can be clamped. A fluid discharge connection 16 is provided and different fluid inlets 20—23. In moulding a leather shoe upper a blank of wet limp skin 10 is clamped by its margins between flanges 12, 19 of the mould container and cover and a dehydrating liquid is admitted through the connection 20 which forces the blank into conformity with the mould and finally passes through the skin and mould to the discharge 16. The blank 10 may be removed in a dry shaped stable state but preferably a liquid tanning agent, a fat liquor, and a dyeing agent may be admitted in turn from the connections 21—23 and passed out of the discharge 16 before the completed upper is removed from the mould. The process is described and claimed in the parent Specification.

Depilatory Paint for Sheepskins and Other Animal Skins. Brit. Pat. 726,842. Zalcman, H. Apl. Feb. 17, 1953. A depilatory paint of the type used to dewool sheepskins

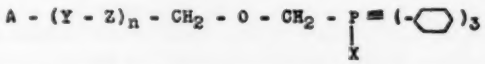
FIG. 2.



consists of an aqueous composition comprising a source of hydroxyl ions selected from the oxides and hydroxides of calcium, strontium, barium, magnesium and sodium, a source of hydrosulphide ions selected from the sulphides and hydrosulphides of calcium, strontium, barium, magnesium, aluminium and sodium, the composition having a sodium ion content within the range of 1 to 60 per cent by weight of the hydrosulphide ion content of the composition, the hydrosulphide and hydroxyl ion content being within the range defined by the area FEBBSSFF of Fig. 2, the composition also containing a reserve source of hydroxyl ions. The preferred *p*H range is 11.5 to 11.9, and the consistency of the composition may be adjusted by the addition of an inert filler such as kaolin. Preferred compositions include calcium hydrosulphide as the source of hydrosulphide ions and this may be prepared by passing hydrogen sulphide into a lime suspension or by reacting aluminium or magnesium sulphides or hydrosulphides with lime. The use of barium or strontium sulphides to provide the hydrosulphide ion is not so desirable since a soluble calcium salt must be added to depress the *p*H by the formation of the corresponding strontium or barium salt, e.g. the chloride. Exemplary compositions are (I) calcium hydrosulphide and lime (or an equivalent composition containing the same hydrosulphide and hydroxyl ion content) to which is added sodium sulphide or hydrosulphide, the former increasing the hydrosulphide ion content and increasing the *p*H, the latter increasing the hydrosulphide ion content, as shown in Fig. 2, where a composition indicated by 1 is obtained by adding sodium sulphide to a calcium hydrosul-

phide/lime suspension indicated by 2, and the composition of point 3 is obtained by adding sodium hydrosulphide to a composition indicated by point 4. (3) Calcium hydrosulphide and lime as shown by point 7 to which has been added sodium hydroxide to raise the *p*H to that shown in point 6. (5) A composition as shown by point 3 to which has been added barium (or strontium) hydroxide to raise the *p*H. The compositions are employed on the flesh side of the skins and the latter are preferably soaked and fleshed before application, thus enabling the depilation to be effected at a lower *p*H. Specification 680,784 is referred to.

Treating Keratinous Fibres. Brit. Pat. 726,936. Geigy Akt.-Ges., J. R. Apl. July 4, 1952. As agents for treating keratinous fibres, particularly wool, furs and feathers, against attack by insects such as beetle larvae and moths, there are specified quaternary phosphonium compounds of the formula



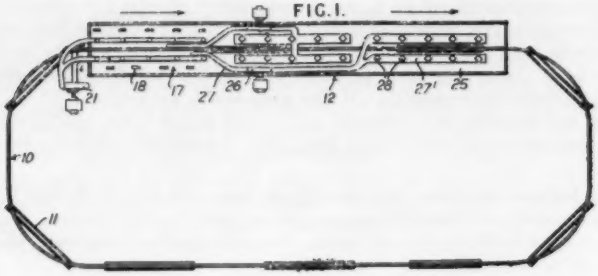
wherein A represents a halogen-substituted radical of the phenyl, diphenylyl or phenoxyphenyl series, Y represents an oxygen or sulphur atom, Z represents an alkylene radical containing 1 to 3 carbon atoms, *n* represents 0 or 1 and X represents halogen, preferably chlorine or bromine. The preparation of such compounds is described (*see* Group IV (b)), examples illustrating the preparation of various compounds of the above formula where A is selected from 2,5-, 3,4-, or 2,4-dichlorophenyl, 4-chlorophenyl - 2,4,5 - , 2,4,6 - or 3,4,5 - trichlorophenyl-, trichlorodiphenylyl-, monochlorodiphenylyl-, and 3 - trifluoromethyl - 4 - chlorophenyl radicals, Y is oxygen or sulpur, Z is methylene, ethylene or propylene and X is chlorine or bromine. In an example: (12) wetted, dyed and undyed wool is treated in aqueous solutions of such compounds at 60° C. and wrung out and dried without rinsing.

Deliming Pelts. Brit. Pat. 728,552. Riverstone Meat Co. Proprietary, Ltd. Apl. April 15, 1953. Pelts are delimed by immersing the limed pelts in an initially lime-free bath containing at least one of the salts: magnesium chloride, magnesium nitrate, magnesium acetate, zinc chloride, zinc nitrate, zinc acetate, aluminium chloride, aluminium nitrate mixed with water. The temperature of deliming is preferably 90—95° F., and after stirring for about one hour the pelts are rinsed in fresh water. The preferred concentrations of the salts in pounds per 500 gallons are respectively 40, 50, 42, 27, 59, 42, 32, 50.

Filling Leather. Brit. Pat. 728,771. Imperial Chemical Industries, Ltd. Apl. Oct. 21, 1953. In a process as described in Specification 583,096 wherein hides and skins are subjected to a tanning operation in conjunction with a drumming operation in an aqueous dispersion of a solid, finely divided polyvinyl chloride or a water-insoluble solid finely divided interpolymer of vinyl chloride with one or more ethylenically unsaturated polymerizable compounds in which vinyl chloride is present in preponderating amounts, the particles in the dispersion are of a size not greater than 0.2μ. A dispersing agent, such as dinaphthylmethane disulphonic acid, may be used to stabilize the polymer dispersion.

Drying Leather. Brit. Pat. 729,145. Kahn, J., and Pier, M. Apl. June 10, 1952. A leather skin is dried and conditioned by securing it by adhesive to a plate, introducing it into a first treatment zone having an air temperature of 350—550° F. wherein it is exposed to infra-red radiation, and then introducing it into a second treatment zone wherein it is ex-

FIG. I.



posed to moving air at a lower temperature, e.g. 200—300° F. for, say, 3—7 minutes. As shown, leather-carrying pairs of plates 11, of enamelled metal, stainless steel or "Monel" metal (Registered Trade Mark) suspended on monorail 10 pass to housing 12 in the first part 17 of which the leather is dried by air circulated downwardly by blower 21 and heated by gas burners 18 which also produce the infra-red radiation. In the second part 25 of the housing, the skins are subjected to the lower temperature air drawn in by blowers 26 through pipes 27 extending into the upper forward portion of chamber 17, and discharged through perforated vertical pipes 28.

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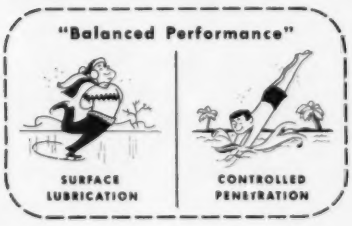

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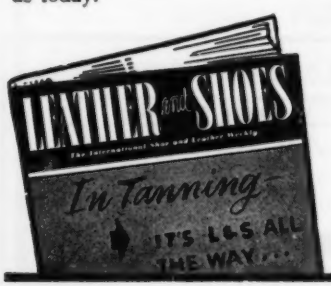

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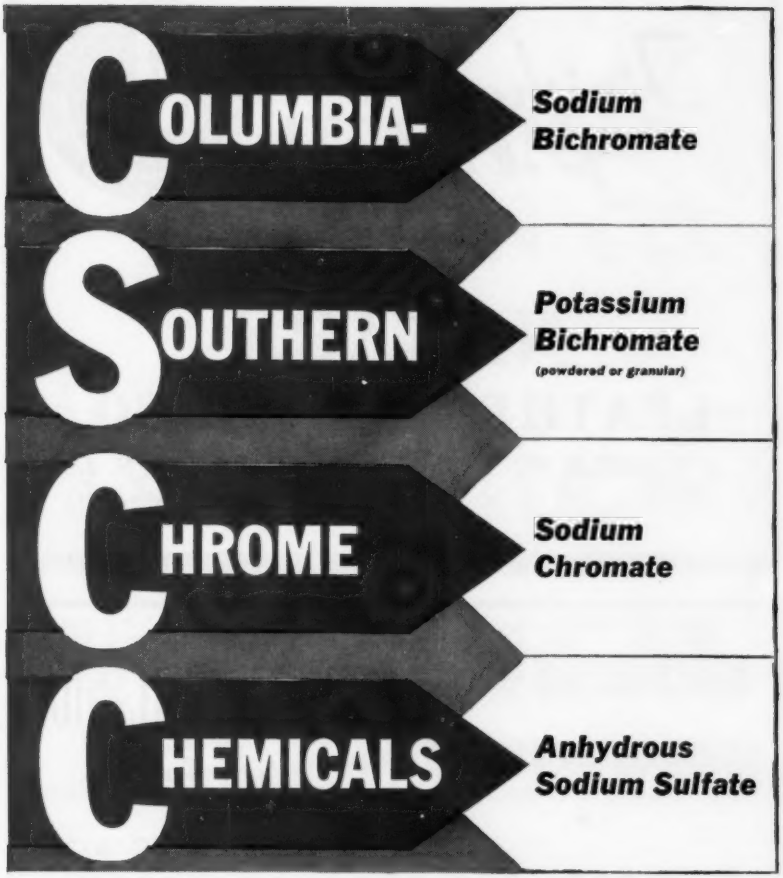

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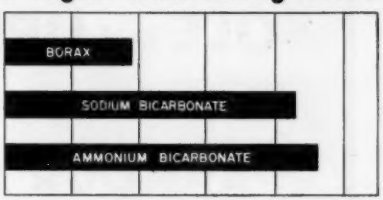
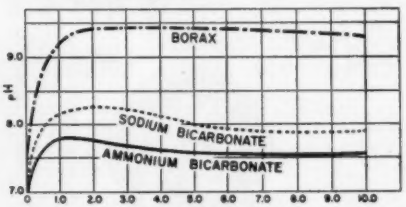


Pounds of hydrochloric acid neutralized by 1 lb. of alkali

2. Lower pH



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